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IMPLICATIONS OF THE VIRIAL THEOREM  
ON THE DESCRIPTION OF WEAK BONDS

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Abstract

The origins of and variations in bonding among weakly bound diatomics are discussed in terms of the virial theorem as applied to Born-Oppenheimer total energy curves. These curves are represented by accurate and flexible analytic functions. Expressions are given for the relations among the parameters of these functions and the electron average kinetic energy,  $\langle T(R) \rangle$ , and the total molecular potential energy,  $\langle V(R) \rangle$ . The relatively brief distance through which weak bonding occurs (as opposed to the relative distances for chemical bonding) is discussed, as is the origin of bond saturation through a homologous series of weakly bound diatomics.



Application of the virial theorem to the total energy of a diatomic molecule within the Born-Oppenheimer approximation yields an instructive and familiar<sup>1</sup> description of the physical origin of bonding between two atoms. If  $W(R)$  is the Born-Oppenheimer total energy of the atoms as a function of separation,  $R$ , then the virial theorem relates the average kinetic energy of the electrons,  $\langle T(R) \rangle$ , and the average Coulombic potential energy of the diatomic,  $\langle V(R) \rangle$ , to  $W(R)$  via the relations

$$\langle T(R) \rangle = -W(R) - R \frac{dW(R)}{dR} \quad (1)$$

and

$$\langle V(R) \rangle = 2W(R) + R \frac{dW(R)}{dR} \quad (2)$$

These three functions are shown in Fig. 1 for the ground state of  $H_2$ , using the ab initio data of Kołos and Wolniewicz<sup>2</sup>.

The distance scale is measured in multiples of the  $H_2$  equilibrium bond length (i.e., the distance,  $R_e$ , at which  $W(R)$  is a minimum), and the energy scale is measured in multiples of the  $H_2$  bond energy (i.e.,  $W(R=\infty) - W(R_e)$ ).

Constants have been added to each curve so that each goes to

zero as  $R \rightarrow \infty$

As the atoms approach, the potential energy rises (electrons are moving away from nuclei) and the kinetic energy falls (as delocalization begins). In the vicinity of  $R/R_e=2$ , this trend reverses. The kinetic energy increases as the electronic wavefunction is localized further, raising the momentum, but the potential energy falls, as charge is now brought nearer both nuclei. Only at  $R/R_e < 0.5$  does nuclear repulsion cause the potential energy to increase and contribute to the total repulsion energy.

These general features apply to any diatomic in a bound state (with the exception<sup>1</sup> of purely ionic attractions). To construct and interpret  $\langle T(R) \rangle$  and  $\langle V(R) \rangle$ , one needs only  $W(R)$ . It has been shown<sup>3</sup> that  $W(R)$  for many weakly bound diatomics can be given accurately by the Thakkar analytic function

$$W(R) = e_o \lambda^2 \left[ 1 + \sum_{n=2}^{\infty} e_n \lambda^n \right] + W(R_e) \quad (3)$$

where  $\lambda = 1 - (R_e/R)^p$  and  $p$  is a positive constant. This function has been shown to represent the true  $W(R)$  throughout the bound region of the molecule, including the long-range attractive tail, in many cases.



In Fig. 2, we show  $W(R)$  for  $\text{Ar}_2$ , using Eq. (3), as well as the  $\langle T(R) \rangle$  and  $\langle V(R) \rangle$  functions derived from it.<sup>4</sup> These functions are plotted in a reduced coordinate system analogous to that used in Fig. 1. All three curves are dramatically different in qualitative appearance from those for  $\text{H}_2$ .

Note that chemical bonding (i.e.  $\text{H}_2$ ) can be attributed to a gradual decrease in  $\langle V \rangle$  throughout a wide portion of the total energy well. Weak bonding can be attributed to the decrease in electron kinetic energy over the attractive tail, but, in the vicinity of  $R_e$ , the roles of  $\langle T \rangle$  and  $\langle V \rangle$  in promoting binding are rapidly reversed.

The behavior of  $\langle T \rangle$  and  $\langle V \rangle$  at long range is, for  $\text{Ar}_2$ , a manifestation of the dispersion interaction. Admixing excited state character to form the wavefunction descriptive of the induced dipole-induced dipole attraction necessarily increases  $\langle V \rangle$  and decreases  $\langle T \rangle$ . (Recall that, for an atom,  $W = -\langle T \rangle < 0$ .) What this analysis shows rather clearly is the persistence of this behavior as  $R$  decreases towards  $R_e$ .

One may take the position of the maximum in  $\langle V \rangle$  or of the minimum in  $\langle T \rangle$  as a lower bound to the inner limit of classical long range attraction. Expressions for these distances (which are slightly different) can be found from

Eq. (1) only by numerical methods, except for the special case  $W(R) = e_o \lambda^2 + W(R_e)$ . This is a simple Lennard-Jones (p,2p) function. For this case, one finds

$$d\langle T \rangle / dR = 0 \quad \text{when } R/R_e = \left( \frac{2p-1}{p-1} \right)^{1/p} \quad (4)$$

and

$$d\langle V \rangle / dR = 0 \quad \text{when } R/R_e = \left( \frac{2p-2}{p-2} \right)^{1/p} \quad (5)$$

Both of these distances are larger than the location of the inflection point in  $W(R)$ , which occurs at  $R/R_e = ((2p+1)/(p+1))^{1/p}$ . Since  $p$  is a property of  $W(R_e)$  and can be calculated<sup>3</sup> from derivatives of  $W(R)$  at  $R_e$ , from observed equilibrium spectroscopic constants, or, as shown below, from first principles, Eq's (4) and (5) provide unambiguous criteria by which one may locate with certainty the "end" of long range attraction as  $R$  is decreased towards  $R_e$ . These relations should be of use in checking the somewhat arbitrary decisions made to locate this point in schemes using piecewise analytic representations<sup>5</sup> of  $W(R)$ .

Several simple and informative relations pertaining to  $\langle V(R_e) \rangle$  and  $\langle T(R_e) \rangle$  can be derived from Eq's (1)-(3). The well-known fact that the decrease in  $\langle V \rangle$  at  $R_e$  is twice the increase in  $\langle T \rangle$  at  $R_e$  is, of course, general, and does not depend on the functional form of  $W(R)$ . Using the following

definitions for derivations of W and for p:

$$k_e \equiv \left( \frac{d^2 W(R)}{dR^2} \right)_{R_e},$$

$$l_e \equiv \left( \frac{d^3 W(R)}{dR^3} \right)_{R_e},$$

and

$$p = -l_e R_e / 3k_e - 1,$$

one finds

$$\left( \frac{d\langle V \rangle}{dR} \right)_{R_e} = - \left( \frac{d\langle T \rangle}{dR} \right)_{R_e} = k_e R_e,$$

$$\left( \frac{d^2 \langle T \rangle}{dR^2} \right)_{R_e} = 3pk_e,$$

and

$$\left( \frac{d^2 \langle V \rangle}{dR^2} \right)_{R_e} = (1-3p)k_e = k_e - \left( \frac{d^2 \langle T \rangle}{dR^2} \right)_{R_e}.$$

Also, for Eq. (3),

$$k_e = 2p^2 e_o (1 + \sum_n e_n) / R_e^2.$$

It is helpful to consider these expressions in reduced coordinates so that the relative variations in  $\langle T \rangle$  and  $\langle V \rangle$

across the bound portion of  $W(R)$  can be compared. Thus, when distances are scaled by  $R_e$  and energies by  $D_e$ , as in the figures, the behavior of  $\langle T \rangle$  and  $\langle V \rangle$  at  $R/R_e=1$  can be related directly to  $p$ , viz.,  $-d\langle T \rangle/dR \sim p^2$ ,  $d^2\langle T \rangle/dR^2 \sim p^3$ , etc.

For chemically bound species,  $p$ 's are found, from spectroscopic data,<sup>6</sup> to lie in the range 0.6 to 3.0. In contrast,  $p$ 's for weakly bound species<sup>3</sup> are found throughout the range 3.1 to  $>6$ . Thus, weak bonds may be characterized in the vicinity of  $R/R_e=1$  as having  $\langle T \rangle$  ( $\langle V \rangle$ ) increase (decrease) at relatively much greater rates than do chemically bound species in general. It is a somewhat surprising outcome of this analysis that weak bonding is a relatively more localized interaction than chemical bonding.<sup>7</sup>

The reason Eq. (3), the Thakkar function, works as well as it does (or, equivalently, fails rather miserably for strongly bound diatomics) appears to involve two factors. The first is the persistence of long range behavior to  $R$  values close to  $R_e$  (see Fig. 2) in many weakly bound molecules<sup>8</sup>, allowing Eq. (3) to reproduce the long range tail with a power series lead by a term in  $R^{-p}$  with  $p$  close to the anticipated integral value.

The second is the physical similarity of repulsive interactions for weakly bound molecules: the Pauli repulsion of two (usually) spherical atoms. Binding, as noted above, is relatively less localized in covalent, ionic, or other strong interactions, and the electron distribution changes less rapidly with  $R$  in the vicinity of  $R_e$ . Eq. (3) accomodates the relatively abrupt repulsion of weakly bound species through the interrelation of  $p$  to  $k_e$  and the derivatives of  $\langle T \rangle$  and  $\langle V \rangle$  noted above.

It is also possible, given the relationship of  $p$  to derivatives of  $W(R)$ , to express  $p$  from first principles. Let  $\psi(r, R)$  be the exact Born-Oppenheimer wavefunction for the diatomic, given as a function of all electron coordinates,  $r$ , and, parametrically, as a function of internuclear distance  $R$ . First, from the Hellmann-Feynman theorem<sup>9</sup>, the internuclear force is given by

$$-\frac{dW(R)}{dR} = -\int \psi^* \frac{\partial V}{\partial R} \psi d\tau = -\langle \partial V / \partial R \rangle. \quad (6)$$

Clinton<sup>10</sup> has derived an expression for  $k_e$  from the virial theorem definition of  $\langle V \rangle$ ;

$$k_{eR_e} = \left( \int \frac{\partial \psi^*}{\partial R} \psi V d\tau \right)_{R_e}.$$

From the differentiation of Eq.(6), one has

$$k_e = \left( \int \frac{\partial \psi^* \psi}{\partial R} \frac{\partial V}{\partial R} d\tau \right)_{R_e} + \left( \int \psi^* \psi \frac{\partial^2 V}{\partial R^2} d\tau \right)_{R_e}$$

From further differentiation of  $\langle V \rangle$ , one has

$$\frac{d^2 \langle V \rangle}{dR^2} = \int \frac{\partial^2 \psi^* \psi}{\partial R^2} V d\tau + 2 \int \frac{\partial \psi^* \psi}{\partial R} \frac{\partial V}{\partial R} d\tau + \int \psi^* \frac{\partial^2 V}{\partial R^2} \psi d\tau$$

When this expression is evaluated at  $R_e$  and combined with the expression for  $(d^2 \langle V \rangle / dR^2)_{R_e}$  given above, one finds

$$\left[ \int \frac{\partial^2 \psi^* \psi}{\partial R^2} V d\tau \right]_{R_e} + \left[ \int \frac{\partial \psi^* \psi}{\partial R} \frac{\partial V}{\partial R} d\tau \right]_{R_e} = -3pk_e = - \left( \frac{d^2 \langle T \rangle}{dR^2} \right)_{R_e}$$

Thus  $p$  can be evaluated from first principles. This expression is also more transparent than the perturbation expression for  $p$  given by Thakkar.<sup>11</sup>

Finally, we note that this expression can be used to find the spectroscopic vibration-rotation interaction constant,  $\alpha_e$ , (or more precisely, the Dunham energy term,<sup>3</sup>  $Y_{11}$ ). This constant leads the expansion of the rotational constant as a function of vibrational quantum number,  $v$ , via

$$B_v = B_e - \alpha_e (v + \frac{1}{2}).$$

From the spectroscopic definition<sup>3</sup> of  $p$ ,

$$p = \frac{\alpha_e \omega_e}{6B_e^2},$$

and the familiar expressions for  $\omega_e$  and  $B_e$  in terms of  $k_e$ ,  $R_e$ ,  $\psi$ , and molecular masses, one can evaluate  $\alpha_e$  from first principles.

One is used to expressing the anharmonic shape of a potential function through the first vibrational correction  $\omega_e x_e$  (or  $Y_{20}$ ). It is important to remember that  $\alpha_e$  not only measures the same effect, but it does so in a more direct fashion. The constant  $\alpha_e$  describes the lengthening (if  $\alpha_e > 0$ ) of the average internuclear separation as the vibrational quantum number is increased.<sup>12</sup>

In conclusion, we apply the results of this analysis to a qualitative view of an aspect of weak bonding which is, at first sight, somewhat unexpected and puzzling. Given the periodic variation of polarizabilities throughout the Periodic Table, one might expect the binding energies of the homologous series  $\text{Ne}_2$ ,  $\text{NeAr}$ ,  $\text{NeKr}$ , and  $\text{NeXe}$  to increase uniformly throughout the series. Instead, the binding energy increases<sup>13</sup> from  $\text{Ne}_2$  to  $\text{NeAr}$ , but then saturates at a virtually constant value from  $\text{NeAr}$  to  $\text{NeXe}$ . Similarly, the greater polarizability of Na when compared to Ar might lead one to predict  $\text{NaAr}$  to be more strongly bound than  $\text{Ar}_2$ .

In fact, NaAr exhibits 40% of the binding energy of  $\text{Ar}_2$ .

Since any of these binding energies is a trivial fraction of the total molecular energy, only very slight and perhaps subtle changes to the separated atom wavefunctions occur near  $R_e$ . Consider first the Ne containing rare gas diatomics. From the measured<sup>13</sup>  $W(R)$ 's, one deduces  $p$  values ranging from 5.3 for  $\text{Ne}_2$  to 5.6, 6.0, and 6.9 for NaAr, NeKr, and NeXe, respectively. This uniform increase in  $p$  implies a uniform (and more pronounced) increase in the rates of change of  $\langle T \rangle$  and  $\langle V \rangle$  near  $R_e$  as Ne is paired with successively larger atoms. The smaller (less polarizable) Ne finds its electrons confined to an even smaller region of space at the onset of repulsive overlap, and the degree of confinement will be greater the larger the other atom happens to be. This will raise the total electron kinetic energy at a rate governed by the identity of the less polarizable atom, in analogy with shortening the length of the box containing a particle in an already short box.

Similar arguments would seem to apply to the alkali metal-rare gas diatomics. The large bond lengths found for these species (i.e.,  $R_e = 5 \text{ \AA}$  for NaAr) imply a repulsive interaction at a distance governed by the spatially diffuse outer  $s$  electron of the alkali. However,  $p$  for NaAr is<sup>3</sup>



$\sim 4.3$ , indicating that the single s electron is, as expected, less effective in raising the kinetic energy of the outer Ar electrons. The near equality of the NeAr-NeXe binding energies and the "anomalously small" binding of NaAr should be regarded as somewhat fortuitous outcomes. But the variations in the detailed shapes of  $W(R)$  near  $R_e$  can be understood in terms of the effects of electron density variations in controlling the repulsive part of  $\langle T(R) \rangle$ .

To summarize, the availability of accurate energy functions for many weakly bound diatomics permits the analysis of weak bonding in terms of the physical consequences of the virial theorem and the detailed shape of  $W(R)$  functions near  $R_e$ . The relatively more abrupt onset of repulsion in weak bonds (compared to true chemical bonds) is traced to the abrupt end of long range attractions and consequent rapid increase in the total kinetic energy of the diatomic's electrons. Periodic variations in non-bonding electron distributions alter the rate of rise of this repulsion in a way which can be measured by the parameters describing the shape of the total energy function near  $R_e$ . These parameters can be directly related to expectation values of the molecular Hamiltonian or to various derivatives of them.

ACKNOWLEDGMENT

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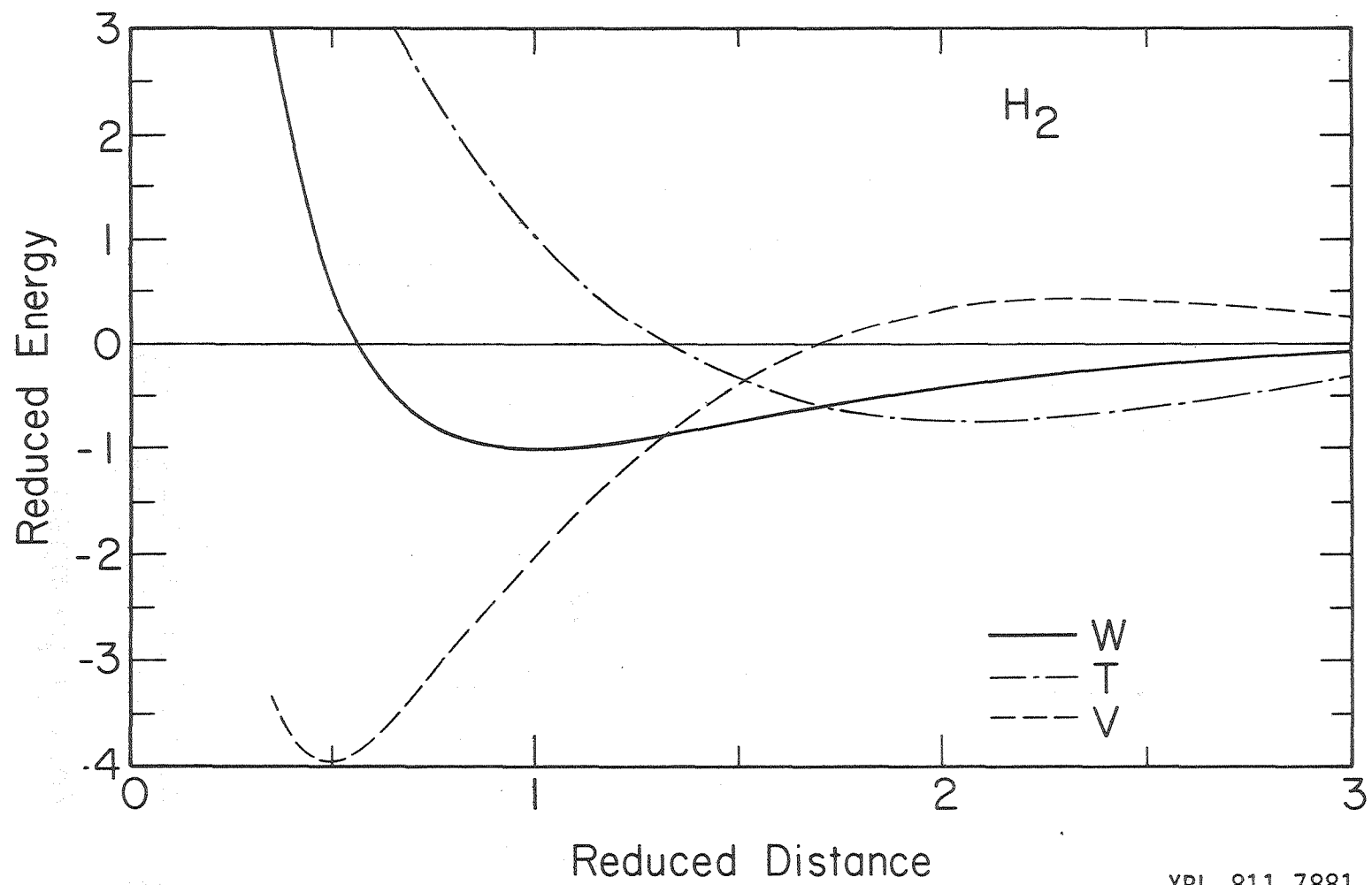
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7. Of course,  $R_e$  is generally larger for weakly bound diatomics than for chemically bound diatomics, and the real distances over which bonding occurs is correspondingly larger.
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10. W. L. Clinton, *J. Chem. Phys.* 33, 1603 (1960). See also P. Phillipson, *J. Chem. Phys.* 39, 3010 (1963).
11. A. J. Thakkar, *J. Chem. Phys.* 62, 1693 (1975). See also R. G. Parr and R. J. White, *J. Chem. Phys.* 49, 1059 (1968).
12. Strictly speaking, the expansion of  $B_v$  about  $B_e$  should be given a classical or semiclassical<sup>v</sup> interpretation here. Thus,  $B_e$  is  $B_v$  for the fictitious level  $v = -1/2$ , and an expansion in powers of  $(v + 1/2)$  should be either mass scaled or reduced to a classical limit of infinite reduced mass.
13. C. Y. Ng, Y. T. Lee, and J. A. Barker, *J. Chem. Phys.* 61, 1996 (1974).

Figure Captions

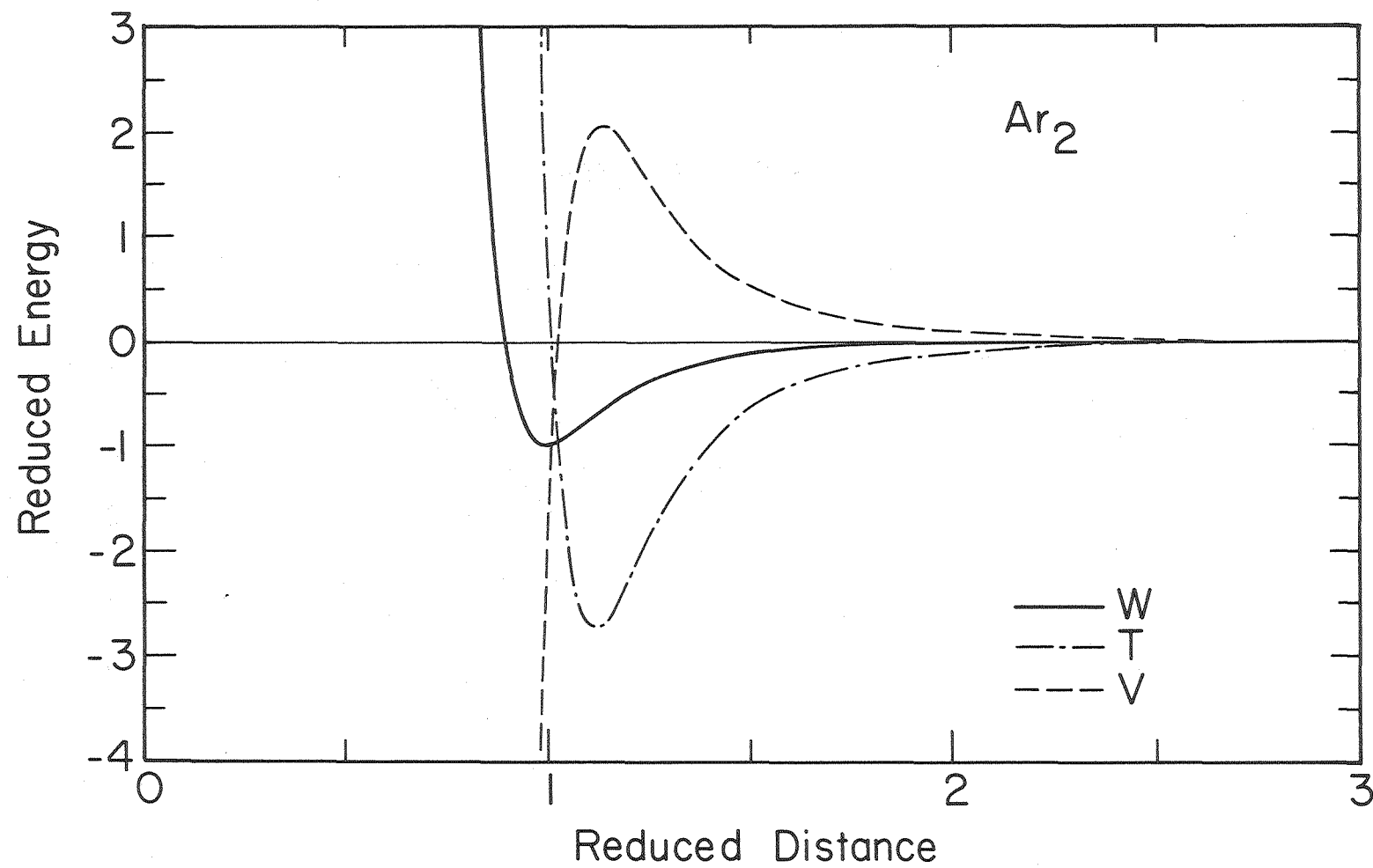
Figure 1. The total energy,  $W$ , the average electron kinetic energy,  $T$ , and the average diatomic potential energy,  $V$ , of  $H_2$ , measured in units of the  $H_2$  bond energy, plotted as a function of internuclear distance, measured in units of the equilibrium  $H_2$  bond length. Data from Ref. 2.

Figure 2. As Fig. 1, but for  $Ar_2$ . Data from Ref. 4.



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Figure 1



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Figure 2